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XIX.

BRIEF CONTRIBUTIONS FROM THE PHYSICAL LABORATORY
OF HARVARD COLLEGE, UNDER THE DIRECTION OF PRO-
FESSOR JOHN TROWBRIDGE.

RELATION BETWEEN SUPERFICIAL ENERGY AND
THERMO-ELECTRICITY.

BY CHARLES BINGHAM PENROSE.

Communicated by Professor Trowbridge, June 11, 1884.

WHEN two media which do not mix are in contact, the particles near the surface have more energy than similar particles in the interior of the media. It is probable that this increase of energy is sensible only within a distance of a thousandth of a millimeter from the surface.

The result of this difference of energy is to render the surface of contact of the media as small as possible. This is seen in Plateau's experiment upon a mixture of oil in alcohol and water.

When the area of the surface is increased in any way the surface energy is increased, and work can be done in the contraction of the surface. The surface behaves exactly as if a tension equal in all directions existed at every point of it. In discussing surface energy it can therefore be considered in two ways. It can be considered as part of the internal energy of the body; and in this case to the internal energy that is generally understood in thermodynamics must be added a term which shall be proportional to the surface, and also a function of the temperature. Or it may be introduced into the equations of the external work: and in increasing the surface it can be said that work is done against superficial tension in the same way that work is done against an external pressure.

The numerical value of the surface energy per unit of area is equal to that of the surface tension per unit of length.

Since the superficial tension depends not only upon the body itself, but also upon the substances in contact with the body, and since work done by, or against, superficial tension depends not merely upon the initial and final states of the body, but upon the manner of passing

from one state to the other, it is probably best to introduce surface energy into the equations of the external work.

Let the state of any body be represented as a function of the two independent variables x and T ,—where T is the absolute temperature. If the body is an homogeneous solid, its mechanical state is represented as a function of six independent variables. The equations, however, deduced by considering only the variations of x and T can be extended to the case of a solid by adding five other equations of the same form.

When the body undergoes any small transformation, the quantity of heat absorbed—expressed in mechanical equivalents—is:

$$dQ = a dx + b dT. \quad (A.)$$

The coefficient “ a ” depends upon the external and the internal works. It is the mechanical equivalent of the latent heat relative to the variable x . $\frac{b}{J}$ represents the specific heat of the body for a constant mechanical state.

The external work is done against superficial tension and external pressure: hence “ a ” depends upon these two quantities.

The value of the external work in the above transformation is:

$$dW = p dx + S dx. \quad (B.)$$

S is a function of the superficial tension and of the shape of the body. The work done against superficial tension is equal to the coefficient of capillarity—or the coefficient of superficial energy—into the increment of area. Let k = the coefficient of capillarity, and let

$$\frac{dA}{dx} = f(x),$$

where A equals the area of the surface of the body. Then for S may be substituted

$$S = k f(x).$$

Let F represent the total energy of the body:

$$dF = a dx + b dT + p dx + S dx. \quad \text{III.}$$

For any closed cycle the total variation of F is zero. The value of an increment of F depends merely upon the initial and final states of the body. dF is therefore an exact differential.

$$\frac{d(a + p + S)}{dT} = \frac{db}{dx} \quad (a.)$$

If the body is supposed to pass through a reversible cycle,

$$\int \frac{dQ}{T} = 0;$$

$$\therefore \int \frac{a dx + b dT}{T} = 0. \quad \text{IV.}$$

Equation IV. only holds if all the steps of the transformation are of a perfectly reversible character, and if the body is finally brought back to its primitive state in every respect. That the part of the transformation depending upon changes in the superficial energy may be considered reversible is shown by the following example:—

- I. Let a soap film be stretched, at temperature T , to area A .
- II. Let it then be cooled to temperature $T - dT$.
- III. Let it then contract at temperature $T - dT$ to its original mechanical state.
- IV. Let it then be heated to temperature T .

Every step of this process is obviously reversible, and the body is finally brought back to its original state in every respect. The work done by the film is equal to that which would have to be done upon it in order to go through the cycle in the reverse direction.

In equation IV. the expression under the integral sign must be an exact differential:

$$\frac{d}{dT} \left(\frac{a}{T} \right) = \frac{d}{dx} \left(\frac{b}{T} \right);$$

substituting from (a),

$$T \frac{d a}{d T} - a = T \frac{d b}{d x} = T \left[\frac{d a}{d T} + \frac{d p}{d T} + \frac{d S}{d T} \right];$$

$$\therefore \frac{d p}{d T} + \frac{d S}{d T} = - \frac{a}{T}.$$

Since $S = k f(x)$,

$$\frac{d k}{d T} = - \frac{1}{f(x)} \left[\frac{a}{T} + \frac{d p}{d T} \right]. \quad (b.)$$

This equation gives the variation of the coefficient of capillarity with the temperature. The experiments of Wolff on the ascent of water in capillary tubes give:

$$k = 76.08(1 - 0.002 T + 0.00000415 T^2),$$

for a tube .02346 cm. in diameter. And

$$k = 77.34(1 - 0.00181 T),$$

for a tube .03098 cm. in diameter.

The equation may also be written :

$$\frac{d p}{d T} = - \frac{d k}{d T} f(x) - \frac{a}{T}.$$

Thomson has shown (Proc. Roy. Soc. Edin., 1870) by considerations regarding the equilibrium between a liquid and its saturated vapor, that the pressure on the surface of the liquid depends upon the form of the surface.

In certain cases the part of the external work, $p d x$, may be considered equal to zero; the chief external work being done against superficial tension. The extension of the soap film represents such a case. Here

$$\frac{d k}{d T} = - \frac{1}{f(x)} \left[\frac{a}{T} \right]. \quad (c.)$$

In considering the case of the soap film mentioned on page 419, it will be seen that the work done against superficial tension in Part I. of the process is

$$2 A k_T.$$

A represents the area, and k_T the value of k for temperature T .

Experiment has shown that the coefficient of capillarity in general decreases as the temperature increases. The work done in the contraction of the film — Part III. of the process — is

$$2 A \left[k_T - \frac{d k}{d T} d T \right].$$

This exceeds the work done upon the film by:

$$- 2 A \frac{d k}{d T} d T.$$

Consequently, from thermodynamic considerations, a certain quantity of heat, Q , must be absorbed at temperature T , and a quantity, $Q - d Q$, must be evolved at temperature $T - d T$, and

$$d Q = - \frac{2 A}{J} \frac{d k}{d T} d T.$$

The second law of thermodynamics gives for this case

$$\frac{Q}{T} - \frac{Q - dQ}{T - dT} = 0;$$

$$\therefore Q dT = T dQ = -\frac{2A}{J} T \frac{dk}{dT} dT;$$

$$\therefore Q = -\frac{2A}{J} T \frac{dk}{dT}.$$

This last equation is a special form of (c). It gives the quantity of heat absorbed in increasing, by A , the area of a film at constant temperature T . The application of Carnot's cycle to this special case was made by Thomson. (Proc. Roy. Soc., IX. 255.) It is obvious that the latent heat of extension of unit of area is equal to the absolute temperature into the decrement of superficial tension per degree of temperature.

Equation (c) may be written :

$$a = -Tf(x) \frac{dk}{dT}.$$

From this form it is obvious that, if $\frac{dk}{dT}$ is minus, there must be an absorption of heat when x is increased, and an evolution when x is diminished.

Experiment has shown that the surface energy between two media is a function not only of the temperature, but also of the difference of electrical potential across the surface. Faraday observed that a large drop of mercury, in contact with dilute sulphuric acid, changed its form when connected with the electrode of a battery. And Lippmann* has made a series of experiments upon the relation between superficial tension and electrical phenomena in the case of mercury in contact with various substances.

The results of Lippmann's experiments may be summed up as follows:—

I. The superficial tension between two liquids is not a specific constant depending merely upon the nature of the substances in contact. The superficial tension is a function of the difference of electrical potential between the two liquids; and for every value of the difference of potential, there is one, and only one, value of the superficial tension.

* Annales de Chimie et de Physique, 1875 and 1877.

II. In the case of mercury — at least in contact with any liquid — the superficial tension is independent of the chemical constitution of the liquid, and depends only upon the difference of potential at the surface. The chemical constitution of a liquid affects the superficial tension only by changing the difference of potential. The experiments of Bloudlot* make it probable that this law can be extended to the case of platinum.

III. When, by mechanical means, the surface of a liquid is deformed, the difference of potential at this surface varies in such a direction that the change in superficial tension developed by the variation of potential is opposed to the continuation of the deformation. This agrees with Lenz's law.

IV. In the case of mercury and dilute sulphuric acid, the superficial tension increases nearly proportionally to the difference of potential; until the difference of potential equals 0.9 Daniell. Any further increase of the difference of potential causes a diminution of the superficial tension.

The experiments of Lippmann explain the cause of the variations observed in measurements of the superficial tension. These variations were first noticed by Quincke† and were attributed by him to the presence of impurities.

Lippmann's experiments show that a close relation exists between contact electricity and superficial tension. This relation may be expressed mathematically as follows: — Let k , as before, represent the coefficient of superficial tension. S represents the area of the surface, and e the difference of potential at the surface; k is a function of e , and is of course independent of S .

If, by the action of any force, the surface is increased by dS , the work done is

$$dW = -k dS.$$

There is at the same time a difference of electrical potential created, the action of which is to oppose the force. An electrical separation takes place across the surface. The quantity, m , of electricity separated is a function of the surface and of the difference of potential:

$$m = \phi(S e),$$

$$dm = X dS + Y de.$$

* Journal de Physique, tom. x.

† Ann. de Poggendorff, vol. cxxxix., 1870.

The consideration of this case may be simplified by a method analogous to that employed in thermodynamics.

In the figure below, let abscissæ represent areas of the surface, and ordinates represent tension per unit-length. Any transformation due to changes in the area and superficial tension of the surface may be represented by a line on the diagram. The work done during the transformation " ab " is equal to the area $aa'b'b$. The area of any closed curve gives the work done during the cyclical process represented by the curve. Since the superficial tension is a function of the difference of potential across the surface, the work will be a function of the difference of potential.

By keeping the liquids on each side of the surface in contact with electrified bodies the difference of potential can be made to vary as we please. The deformation of the surface, due to any force, may be made to take place at constant, or at variable potential.

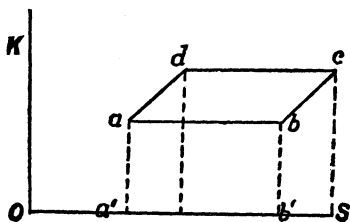
A special form of cyclical process may be arranged such that the transformations take place only in two ways. In one way the liquids are kept in contact with conductors of infinite capacity and constant potential; in the other way they are insulated. The line representing a transformation according to the first way is parallel to OS , and electrical energy must either leave or enter the liquids. For in order to keep the difference of potential constant, when it tends to increase, electrical energy must leave the surface of contact of the liquids; and when the difference of potential tends to diminish electrical energy must be furnished to the surface.

As in thermodynamics any cycle can be considered to be made up of isothermal and isentropic lines, so in the present case any cycle may be considered to be made up of lines of constant potential, and lines of variable potential.

Let the cycle in the figure be composed of two lines of constant potential, and two lines of variable potential.

Along the line ab work is done in increasing the area of the surface. By III. of Lippmann's results, the difference of potential tends to increase, and k tends to increase. To keep the difference of potential constant electrical energy, E_1 , must leave the liquids.

Along the line bc work is done upon the surface; and the difference of potential and k are increased. No energy of any kind is allowed to



enter or leave the liquids. Along the line cd the surface contracts and does work at the constant increased difference of potential. The tendency of the difference of potential along cd is to diminish, and to keep it constant electrical energy, E_2 , must enter the liquids.

Along da the surface contracts and the difference of potential and superficial tension diminish to their original values.

The liquids, after this process, are in every respect in their primitive condition; and the difference of potential across the surface being the same, the total quantity of electricity upon the surface must be the same as at the beginning of the process.

It is obvious from Lippmann's results that the cycle is also completely reversible. Since during the cycle there is a gain of work $abcd$, the electrical energy which enters the liquids must be greater than that which leaves them, and we have

$$abcd = E_2 - E_1.$$

As the liquids are conductors, the only place at which a difference of potential exists, in the whole body, is at the surface of separation. The quantities of electricity entering and leaving the body, do so at this difference of potential.

Let P_1 and P_2 represent the differences of potential for the lines ab and cd respectively.

$\frac{E_1}{P_1}$ is proportional to the quantity of electricity Q_1 which leaves the liquids along ab .

$\frac{E_2}{P_2}$ is proportional to the quantity Q_2 which enters the liquids along cd .

Since the total quantity of electricity upon the surface is the same at the end of the process as at the beginning,

$$Q_1 = Q_2,$$

$$\therefore \frac{E_2}{P_2} - \frac{E_1}{P_1} = 0.$$

As any cycle may be decomposed into special cycles like the one that has been considered, we have for the most general case,

$$\int dE = W = - \int k dS, \quad \text{V.}$$

$$\int \frac{dE}{P} = 0 = \int dm. \quad \text{VI.}$$

The electrical cycle that has been considered would probably be found useful in the investigation of many similar problems, where electrical energy is transformed into mechanical work.

The analogy between the equations V. and VI. and those derived from the two laws of thermodynamics is very close.

The equations might have been obtained by accepting immediately the theory of the conservation of electricity.*

Since

$$dE = P dm = e dm,$$

equation IV. may be written

$$\int e dm = - \int k dS;$$

$$\therefore \int (e dm + k dS) = 0.$$

Substituting the value of dm ,

$$\int (e Y de + e X dS + k dS) = 0.$$

As the expression under the integral sign is an exact differential,

$$\frac{d(eX + k)}{de} = \frac{d(eY)}{dS}.$$

X obviously represents the electrical capacity of unit surface at constant potential.

Y is the electrical capacity of the whole surface, as the potential varies. If C is the capacity for unit surface

$$Y = CS.$$

The last equation reduces to

$$e C = \frac{d(eX + k)}{de}. \quad (d.)$$

From equation VI.,

$$\int dm = 0,$$

$$\int (CS de + X dS) = 0.$$

This expression being also an exact differential,

$$C = \frac{dX}{de}. \quad (e.)$$

* Lippmann, Journal de Physique, tom. x.

By combining equations (e) and (d) we obtain

$$X = -\frac{dk}{de} \text{ and } C = -\frac{d^2k}{de^2};$$

and dm may be written

$$dm = -d \left[S \frac{dk}{de} \right].$$

These equations were obtained by Lippmann. They show the close relation existing between contact electricity and superficial tension. The equations contain all the results of Lippmann's experiments; and though these experiments were made only upon special substances, yet it seems probable that the conclusions can be extended to all substances.

If the electrical charge for any transformation is kept constant,

$$O = CSde + XdS;$$

$$\frac{de}{dS} = -\frac{X}{CS} = -\frac{-\frac{dk}{de}}{-\frac{d^2k}{de^2}S}.$$

From Section IV., page 422, it is seen that $\frac{dk}{de}$ is plus below a certain value of e for mercury. As the curve representing the change of k with e is concave toward e , $\frac{d^2k}{de^2}$ is minus. Hence $\frac{de}{dS}$ is plus, or below a certain limit the difference of potential increases as the area of the surface increases.

Substances which do not act chemically on each other follow Volta's tension law. In any closed circuit at uniform temperature the sum of the differences of potential between the elements of the circuit is null. From II. of Lippmann's experiments is obtained a simple method of finding the superficial tension between two liquids, which do not act chemically upon each other, when we know the superficial tension between each of these liquids and a third liquid.

Let the contact electromotive forces between AB , BC , CA , be e_1 , e_2 , e_3 , respectively. Let k_1 , k_2 , k_3 be the superficial tensions corresponding to these differences of potential.

Also,

$$k_1 = \phi(e_1) \therefore e_1 = \phi^{-1}k_1.$$

$$e_2 = \phi^{-1}k_2 \text{ and } e_3 = \phi^{-1}k_3.$$

Since

$$e_1 + e_2 + e_3 = 0,$$

$$\phi^{-1} k_1 + \phi^{-1} k_2 + \phi^{-1} k_3 = 0;$$

$$\therefore k_3 = -\phi [\phi^{-1} k_1 + \phi^{-1} k_2].$$

Suppose we have a vertical glass tube, the lower half containing mercury and the upper half dilute sulphuric acid. Suppose the + pole of a battery, the electromotive force of which does not exceed 0.9 Daniell, is connected with the acid, and the — pole with the mercury. The superficial tension is increased and there is a contraction of the surface. From equation (c) a quantity of heat Q is evolved:

$$Q = -T \frac{dk}{dT} dS.$$

If the poles of the battery are reversed there will be an absorption of heat of the same amount. If the difference of potential exceeds 0.9 Daniell the effects will be reversed.

This is completely analogous to the Peltier phenomenon on each side of a neutral point.

If the surface of separation between mercury at constant potential and dilute sulphuric acid at constant higher potential is increased by the action of any force, work is done against superficial tension, and the energy of electrical separation appears. Positive electricity is separated across the surface from mercury to acid; and the tendency of the electrical action is to oppose the force. Conversely if the energy of electrical separation disappears by the passage of positive electricity from the acid to the mercury, mechanical work is done against superficial tension by dilatation of the surface.

Suppose we have a bent glass tube of uniform bore, containing dilute sulphuric acid in the bent part, and a column of mercury in each arm A and B . Let the temperature of the meniscus at A be T , and that of the meniscus at B be $T - dT$. Let the potential of the sulphuric acid be maintained constant, by any means, and equal to V .

Let the mercury at B be put in contact with a conductor of constant potential V_1 , and infinite capacity. Let the mercury at A be put in contact with a similar conductor at potential V_2 .

Let these potentials be so arranged that the change in the difference of potential at B is equal and opposite to that at A .

If the difference of potential at B is increased an electrical separation takes place so as to produce a contraction of the surface. At A

the separation takes place so as to produce a dilatation of the surface. The electrical change causes an evolution of heat at B , and an absorption of heat at A .

For the present it will be assumed that the superficial tension is a function of the temperature.

The electrical works at A and B are equal and opposite.

Since, however, the superficial tensions at the two surfaces are different, the changes in the areas of these surfaces, though opposite, are not equal.

Let dS_A equal the increment of area at A . Let dS_B equal the increment of area at B .

The work done at A is

$$-k dS_A.$$

The work done at B is

$$-\left(k - \frac{dk}{dT} dT\right) dS_B.$$

Since these works are equal,

$$dS_A = \left[1 - \frac{1}{k} \frac{dk}{dT} dT\right] dS_B.$$

The quantity of heat absorbed during the expansion dS_A is

$$\begin{aligned} Q_A &= -T \frac{dk}{dT} dS_A, \\ &= -T \frac{dk}{dT} \left[1 - \frac{1}{k} \frac{dk}{dT} dT\right] dS_B. \end{aligned}$$

The quantity of heat given out during the contraction dS_B is

$$\begin{aligned} Q_B &= (T - dT) \left[\frac{dk}{dT}\right] dS_B, \\ &= T \frac{dk}{dT} dS_B - dT \frac{dk}{dT} dS_B. \end{aligned}$$

$$\therefore Q_A + Q_B = \left[T \left(\frac{dk}{dT}\right)^2 dT - dT \frac{dk}{dT}\right] dS_B.$$

As long as $\frac{dk}{dT}$ is minus, the right-hand member of this equation is essentially minus, and there is consequently more heat absorbed than evolved.

If the direction of the change of potential were reversed, the above expression would represent the excess of heat evolved at the hot surface over that absorbed at the cold surface.

In the case under consideration a difference of potential is created, and an electrical displacement takes place throughout the tube. Let e equal the total electromotive force, and dm the displacement.

Let R equal the electrical resistance.

$$e dm = R dm^2 + (Q_A + Q_B) J.$$

Let

$$(Q_A + Q_B) J = d\theta \cdot dS_B.$$

We have seen that

$$dm = -X dS_B,$$

for a constant difference of potential ;

$$\therefore e dm = R dm^2 - d\theta \cdot \frac{1}{X} dm ;$$

$$\therefore dm = \frac{e + \frac{d\theta}{X}}{R}.$$

This equation shows that the electromotive force e is supported by an electromotive force $\frac{d\theta}{X}$. This electromotive force is due to the difference of temperature between A and B , and is maintained by the absorption of heat at the warmer surface.

Let this electromotive force be represented by dE ;

$$XdE = d\theta.$$

From the definition of $d\theta$,

$$\frac{d\theta}{dT} = \left[\frac{T}{k} \left(\frac{dk}{dT} \right)^2 - \frac{dk}{dT} \right] = X \frac{dE}{dT}.$$

We have seen that $\frac{dk}{dT}$ is of the form,

$$\frac{1}{f(x)} \left[\frac{a}{T} \right],$$

$$\therefore \frac{dE}{dT} = \frac{a}{f(x)X} \left[\frac{a}{kf(x)} - 1 \right] \frac{1}{T}.$$

This equation shows that the variation of the secondary electromotive force — the electromotive force peculiar to the arrangement — with the temperature, is inversely proportional to the temperature.

The analogy between this thermo-electromotive force, which is caused by a change in the superficial energy, and the electromotive force of an ordinary thermo-electric circuit, is thus very close. It will be remembered that for a thermo-electric circuit

$$\frac{dE}{dT} = \frac{\pi}{T}.$$

If we accept the conclusion of Lippmann,* that the temperature alters the superficial tension only by altering the difference of potential, we can consider the superficial tension only as a function of the difference of potential, and the difference of potential as a function of the temperature.

$$\begin{aligned} \frac{dk}{dT} &= \frac{dk}{de} \cdot \frac{de}{dT}, \\ &= -\frac{1}{f(x)} \left[\frac{a}{T} \right], \\ \therefore \frac{de}{dT} &= -\frac{1}{f(x)} \cdot \frac{a}{T} \cdot \frac{1}{\frac{dk}{de}}. \end{aligned}$$

This expression is also of the same form as the one already obtained; and shows that the variation of the difference of potential with the temperature is inversely proportional to the temperature.

In the case of mercury and sulphuric acid, $\frac{dk}{de}$ is + up to a certain point, after which it is —. Consequently, for this case, $\frac{de}{dT}$ is + up to a certain point, and is afterwards —. This is the same as the variation of the electromotive force of a thermo-electric circuit, on each side of a neutral point.

The cases already considered point to a close relation between superficial energy and the energy of a thermo-electric current. In the first case, however, a continuous current could be maintained only by rapid changes, or vibrations, in the surface of separation of the mercury and acid.

By considering the area of the surface to remain unchanged, and by investigating only the changes in the potential energy of the sur-

* Annales de Chimie et de Physique, 1877, p. 275.

face, caused by variations of temperature, similar results may be obtained without the aid of Lippman's experiments.

It will, for the present, be assumed that the superficial tension decreases as the temperature increases.

When any surface of constant area is heated, a certain amount of superficial energy disappears. It must be converted into some other form of potential energy. This other form of energy can be made to reappear, as heat, in the contraction of the surface. Equation (c) shows that the evolution of heat varies directly with the temperature of the surface.

If therefore we consider unit surface at temperature T , we can find the total amount of energy in the surface by making it contract to nothing at constant temperature T .

The total heat in the body upon which the surface considered exists, is

$$\int_0^T \sigma dT + T \frac{dk}{dT} \frac{1}{J},$$

where σ equals the total specific heat before the formation of the surface. When this surface disappears the total heat is diminished by

$$T \frac{1}{J} \frac{dk}{dT}.$$

The total energy is further diminished by an amount equal to the potential energy of superficial tension of the surface.

The total potential energy of any surface is, therefore, equal to the potential energy of superficial tension plus another form of potential energy, which appears as heat in the contraction of the surface. Hence, what we have previously understood as superficial energy is but a part of the total energy of any surface.

Let k equal the superficial tension at temperature T . Let q equal the mechanical equivalent of the heat evolved in the contraction of unit surface to nothing. Let P equal the total energy of unit surface.

$$P = k + q. \quad (f.)$$

The following consideration is based upon the fact that this value of P for any surface is independent of the temperature. This can easily be seen by considering the cycle on page 419. If k_1 and q_1 are the values of k and q at the higher temperature, and k_2 and q_2 their values at the lower temperature,

$$k_2 - k_1 = q_1 - q_2,$$

$$\therefore k_1 + q_1 = k_2 + q_2 = P.$$

The electrical separation at a hot surface is, in general, greater than that at a cold surface. Consequently, when the temperature of a surface is raised, a certain amount of potential energy of electrical separation appears. At the same time a quantity of potential energy of superficial tension disappears. Moreover, as the surface contracts to nothing, potential energy of electrical separation disappears and the energy of heat appears. If the surface is kept constant, and no energy is allowed to enter or leave it, the electrical energy developed by a change of temperature must be equal to the decrease in k , and to the increase in q of equation (f).

The energy of electrical separation for an increment of temperature dT is consequently

$$- \frac{dk}{dT} dT,$$

for unit surface.

If the two sides of the surface are electrically connected, the electrical separation disappears. Nevertheless the value of P must remain constant; and the energy which leaves the surface must be replaced by an equal amount of energy which can only be derived from the heat at the surface.

Consider that the two ends of a horseshoe-shaped platinum bar, $A B$, are surrounded by a glass tube, $A C B$, containing dilute sulphuric acid. The areas of the surfaces of contact of platinum and acid are constantly equal to unity.

In the beginning let the whole apparatus be at temperature T . The total surface energies of A and B are equal, and consist of two parts which are respectively equal. The potential energy of superficial tension is the same at each surface; and the electrical energy is the same, since there is electrical equilibrium.

Let the temperature of A be increased by dT .

The total surface energy at A is still unchanged — aside from the mere increase of heat — but the components of the total energy are different. There is less energy of superficial tension, and greater energy of electrical separation. Since the circuit is composed of conductors there will be an establishment of electrical equilibrium; and the electricity separated at A from platinum to acid, will flow toward the right. To maintain the value of P at the surface A constant, heat must be absorbed, and a steady current will thus be produced.

Moreover, it is obvious that heat will be evolved at the surface B . For the heat evolved when the surface contracts to nothing is due to the disappearance of the energy of electrical separation; the electricity flowing back in a direction opposite to that in which it was first separated.

Consequently, if electricity is separated from platinum to acid, heat will be evolved when it flows from acid to platinum.

The energy of electrical separation that takes place at any instant is

$$-\frac{dk}{dT} dT.$$

The current strength into the electromotive force equals the electrical energy, and this is maintained by a disappearance of heat which must be proportional to

$$\frac{dk}{dT} dT \Sigma dm,$$

Σdm being the total quantity of electricity separated in unit time. A current of unit strength would consequently absorb an amount of heat:

$$-\frac{dk}{dT} dTM = \theta dT.$$

The arrangement considered forms a reversible thermodynamic engine. For small currents we can therefore consider the heat absorbed as proportional to the first power of the current strength.

The heat absorbed by a current dm is

$$\theta dm dT.$$

The energy of the current must equal the heat absorbed:

$$de \cdot dm = \theta dm \cdot dT,$$

$$\therefore \frac{de}{dT} = \theta = -\frac{dk}{dT} M.$$

From equation (c.)

$$\frac{de}{dT} = -\frac{1}{f(x)} \left[\frac{a}{T} \right] M = \frac{\phi}{T}.$$

For a circuit in which the temperatures of the junctions differ by a finite amount,

$$e = \int_{T_0}^T \frac{\phi}{T}.$$

The expression ordinarily obtained for the electromotive force of a thermo-electric circuit is

$$E = \int_{T_0}^T \frac{\pi}{T}.$$

The only assumption made in obtaining this equation was that the heat effects obey the two laws of thermodynamics.

It is thus seen that the same form of fundamental equation can be obtained in an entirely different way, by considering the energy of a thermo-electric current as part of the energy which resides upon every surface.

The last case is, in every respect, identical with the ordinary thermo-electric circuit between a solid and liquid. And if the results of Lippmann are accepted it has been shown that even the existence of neutral points can be explained.

If, as Maxwell says, there is for all bodies a coefficient of superficial energy, the energy of every thermo-electric circuit may be accounted for by changes in the potential energy of superficial tension.